Plasma-Based Functionalization of Graphene

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ABSTRACT

Graphene is the subject of intense research because of its unique structural and electronic properties, which are advantageous in a large number of applications including nano-electronic and sensing devices. It is thought that, by varying the surface chemistry of graphene, the electronic properties of the material and the interaction with adsorbates can be controlled. In this work, we discuss adding fluorine groups to the surface of graphene, using electron beam generated plasmas. These novel plasma sources are characterized by low electron temperatures (< 1 eV) and thus low incident ion energies at the substrates, features that are critically important when processing very thin substrates like graphene. The results of experimental investigations using these plasmas produced in Ar/SF_6 mixtures in an effort to introduce fluorine functional groups are presented. A study of the chemical and structural properties of the functionalized graphene by X-ray photoelectron spectroscopy and Raman spectroscopy will be discussed.

INTRODUCTION

Pure graphene is well known to be a promising material [1-5] due to its superior properties which includes: high thermal conductivity, high mechanical properties, and high charge carrier mobility. However, to integrate graphene in devices one needs to control its properties. The changes in the electronic structure caused by orbital hybridization are expected to produce large changes in its properties (conductivity, reactivity towards chemicals, mechanical properties, etc.). In this work, the functionalization of graphene with fluorine using electron beam generated plasmas produced in Ar/SF_6 gas mixtures will be presented. It is known that the addition of fluorine to carbon compounds, increases its hydrophobicity [6, 7], lowers its surface energy [7] and is useful in bio-applications [8].

The key attributes of electron beam generated plasmas is that they offer high plasma densities (10^{10}-10^{11} cm^{-3}) along with low electron temperatures (< 1 eV). These features are particularly important in the processing of very thin and sensitive materials such as graphene since this technique allows the addition of functional groups without appreciable etching or altering the graphene lattice via ion bombardment.

After functionalization, the samples were annealed in order to reduce them back to graphene. This reversibility demonstrates the ability to functionalize graphene without significantly damaging it, and is required in several applications, such as, circuitry printing [9] and energy storage.

EXPERIMENTAL

The experimental apparatus, shown in Figure 1, has been described in detail elsewhere [10]. Briefly, electron beams were produced by applying a -2 kV pulse to a linear hollow cathode. The electron beam passed through a slot in a grounded anode (slotted anode) and terminated at a second grounded anode (termination anode). The electron beam was confined by applying a magnetic field of 150 Gauss produced by a Helmoltz coil located outside the chamber. The confinement of the electron beam resulted in a uniform electron sheet and thus ionization volume between the two anodes. The distance between anodes (60 cm) and the slot length (25 cm) define the plasma sheet and thus potential substrate area. The processing stage was located at 2.5 cm from the electron beam axis. The base pressure (~10^{-7} Torr) in the chamber is maintained by a turbo molecular pump. Argon and SF_6 were introduced through mass flow controllers and the desired operating pressure (50 mTorr) was achieved by throttling the turbo pump with a conductance limiter. The amount of SF_6 was limited to 5% of the total flow rate of 50 sccm. The plasma was operated at a duty factor of 10% (2 ms pulse width and 20 ms period) and the total treatment time was 60 seconds (plasma exposure time was 6 seconds). It should be noted that the plasma processing was performed at room temperature.

Graphene was produced by CVD growth on copper as described in [11]. The graphene was then transferred to a Si/SiO_2 substrate and placed into the vacuum chamber for plasma treatment. After treatment, the functionalized graphene was annealed in a Rapid Thermal Annealing processing furnace (Axic, Inc.) at 500°C in Ar for 10 minutes. *Ex situ* surface diagnostics were performed on the as-grown graphene, functionalized graphene and on the annealed functionalized graphene. The chemical composition of the samples was identified by XPS (K-Alpha, Thermo Scientific). The structure of the samples was examined by Raman spectroscopy (Renishaw InVia Raman microscope, 514.5 nm diode laser excitation).

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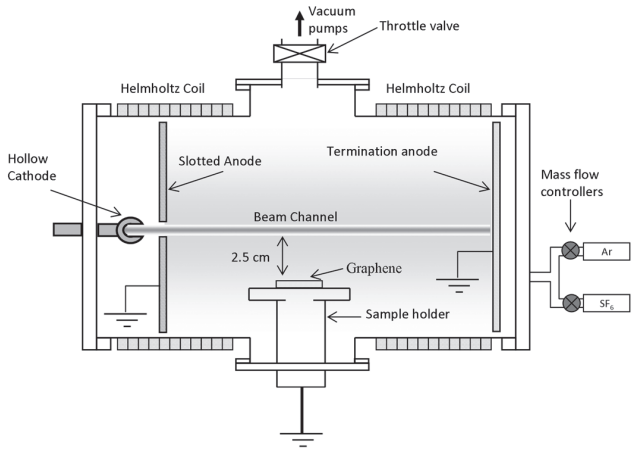

Figure 1: A schematic diagram of the processing system.

RESULTS AND DISCUSSION

The characteristics of the SF_6 containing electron beam generated plasmas are well documented [12]. In Figure 2, the ion energy distributions of Ar^+ and SF_5^+ ions incident to an electrode located adjacent to e-beam generated plasmas produced in Ar/SF_6 gas mixtures are presented. When graphite is exposed to Ar^+ ions bombardment, the penetration and displacement thresholds have been estimated to be between 30 and 50 eV [13, 14]. From these measurements, the average ion energy is around 3 eV and does not exceed 5-6 eV for both Ar^+ and SF_5^+ ions, which is well below the threshold of creation of defects in graphite. However, these energies are sufficient to drive chemical reactions at the surface when reactive species are present. Thus, the introduction of functionalities should proceed without altering or etching the graphene.

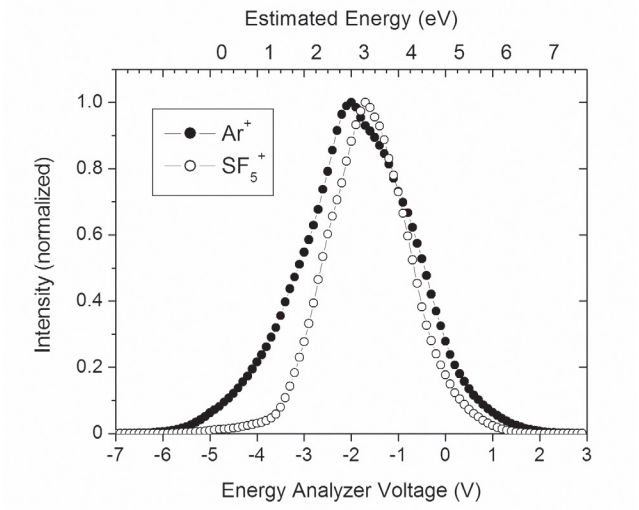

Figure 2: Energy distribution of Ar and SF_6 ions present in electron beam generated plasmas produced in Ar/SF_6 *gas mixtures.*

Chemical changes introduced via plasma treatment are easily observed by examining the XPS high resolution spectra of C1s core level. The as grown graphene in Figure 3a exhibits the presence of C-C sp^2 bond at 284.4 eV. The asymmetry in the peak is associated with the presence of oxygen incorporated during handling or transfer to the Si/SiO_2 substrate. After graphene is exposed to Ar/SF_6 plasmas, the C1s high resolution spectra presented in Figure 3b shows the incorporation of fluorinated functionalities: C-CF, C-F and C-F_2 bonds.

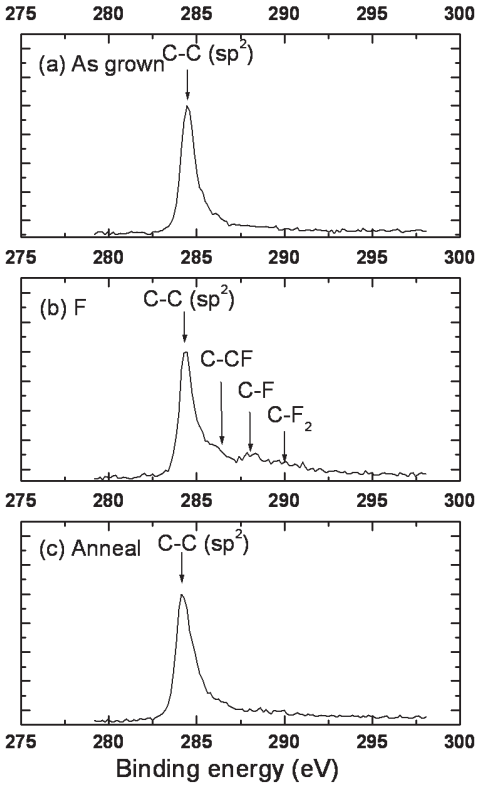

Figure 3: C1s XPS spectra for (a) as-grown, (b) fluorine-modified and (c) annealed graphene.

The graphitic structure of graphene is formed of hexagonal rings of sp^2-hybridized carbon. The G band is observed around 1600 cm^{-1} in the Raman spectrum of the as-grown material (Figure 4a). One does also notice the presence of a D band, which in this case can arise from imperfections associated with discontinuities in the graphene film likely associated with the previously discussed handling/transfer. It is also worth noting the presence of a G band (also called 2D band), around 2680 cm^{-1} (not shown). After plasma treatment a clear change in the Raman spectrum is seen (Figure 4b) and associated with addition of functional groups. Upon incorporation of fluorine sp^3 hybridization occurs due to the creation of covalent bonds with carbon [15]. Thus, the observed increase in the intensity of the D band, which indicates a rising amount of the sp^3 bonded carbons, is due to chemical functionalization of the

graphene structure with fluorine. The D to G intensity ratio of the samples before and after functionalization are 0.2 and 1.5, respectively.

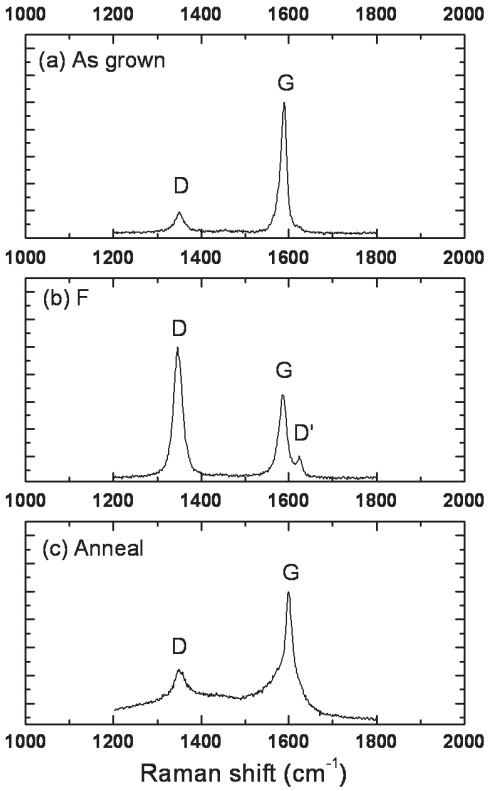

Figure 4: Raman spectra for (a) as-grown, (b) fluorine-modified and (c) annealed graphene.

After annealing, the species adsorbed and the defects created by the functionalization are removed, as indicated in the XPS and Raman spectra shown in Figures 3c and 4c. A decrease in the D to G ratio is observed (from 1.5 to 0.5). The reduction of the modified graphene back to graphene at temperatures as low as 500°C, is an indication of the minimal damage to the graphitic backbone structure which is made possible through the low ion bombardment energy in electron beam generated plasmas. On the other hand, the broadening observed in the D and G peaks (Figure 4c) are associated with the defects and vacancies created [16] upon the removal of carbon with fluorine, since it is known that CF_n compounds (primarily CF) will desorb from graphite [17, 18].

CONCLUSION

In summary, electron beam generated plasmas produced in different gas mixtures is an effective tool for the functionalization of graphene films. Fluorine was added to graphene and verified by XPS and Raman spectroscopy. The reduction back to graphene, by annealing at low temperatures, demonstrates the ability to functionalize graphene without altering its structure. The flexibility of the system described here, allows the addition of a broad range of functionalities by simply varying the operating gas. Chemically functionalizing graphene with electron beam generated plasmas, characterized by low ion energies and large surface areas, expands the utility of these materials and offers a direct path to processing on the industrial scale.

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